



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US89/04721 (22) International Filing Date: 23 October 1989 (23.10.89) (30) Priority data: 261,793 24 October 1988 (24.10.88) US (71) Applicant: HANDY & HARMAN [US/US]; 850 Third Avenue, New York, NY 10022 (US). (72) Inventor: BEEFERMAN, Dennis ; 17985 Colline Vue Blvd., Brookfield, WI 53005 (US). (74) Agent: JONES, Harry, C., III; Pennie & Edmonds, 1155 Avenue of the Americas, New York, NY 10036 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report.</i>
(54) Title: BRAZING PASTE FOR JOINING MATERIALS WITH DISSIMILAR THERMAL EXPANSION RATES (57) Abstract A brazing paste for brazing together materials having dissimilar thermal expansion rates which includes a powdered metal brazing alloy, powdered metal spacer spheres, an inorganic flux and a binder material. The spacer spheres are ductile metal which is not drawn into solution by the brazing alloy during the brazing operation and thereby provides a buffer which absorbs thermal stresses generated by the different materials upon cooling the joint. The brazing paste according to the present invention is equally well suited for brazing operations using directly applied heat, for example torch or induction.		

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BRAZING PASTE FOR JOINING MATERIALS WITH
DISSIMILAR THERMAL EXPANSION RATES

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BACKGROUND OF THE INVENTION

The invention relates to brazing alloys and more particularly to a brazing paste for brazing together materials with dissimilar thermal expansion properties.

10 In the brazing together of dissimilar materials such as tungsten carbide and steel, diamond and steel or in electrical contact applications, problems arise due to the dissimilar coefficients of thermal expansion of the materials. Upon cooling the joined parts after brazing, stresses develop due to the different expansion rates.
15 These thermal stresses can cause cracks in the joint limiting joint performance and possibly leading to ultimate failure.

In the area of carbide-steel brazing a number of solutions have been proposed. U.S. Patent No. 4,340,650
20 discloses a three-layer solid brazing sheet with a layer of ductile metal sandwiched between two layers of brazing alloy. The ductile center has a melting point higher than the melting point of the brazing alloy and helps to absorb thermal stresses as the joint is cooled. While good
25 results have been achieved using this type of brazing sheet it has a significant disadvantage as compared to brazing pastes. The sheet must be stamped, cut or otherwise formed to the shape and size of the parts being joined. This entails additional fabricating steps and may necessitate a
30 large inventory of preformed brazing sheets. An additional drawback is that such preforms are not well suited for high volume production brazing because they must be placed and temporarily secured on the parts to be joined.

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Brazing pastes have the distinct advantage of adapting to any shape, eliminating the need for an inventory of preforms, and they may be applied by existing automated paste dispensing equipment. In an attempt to combine the advantages of the brazing alloy sheet with those of a brazing paste, U.S. Patent No. 4,431,465 provides a mixture of powdered metal brazing alloy and a small quantity of ductile powdered metal with a higher melting point in a water soluble resin. This mixture forms a paste-like substance for brazing tungsten carbide to steel wherein the ductile powdered metal provides a buffer between the joined parts to alleviate thermal stress. However, this brazing paste compound has the disadvantage that the brazing must be done in an oven under a vacuum. This requirement severely limits the commercial practicality of the brazing paste because the majority of commercial brazing is done by torch or induction at atmospheric pressure. Another drawback of this paste is that it contemplates the use of metals, such as nickel or copper, for the buffer which could be drawn into solution by the brazing alloy at temperatures below the actual melting point of the buffer metal. This would result in a loss of buffer material causing the gap between the parts joined to be decreased and thereby degrading joint performance.

Another application in which the difference between the thermal expansion rates of the materials being joined causes problems is the brazing together of diamond and steel. U.S. Patents No. 4,560,853 and No. 3,856,480 provide brazing materials for joining diamond and steel which include metal powders, but these patents are directed to other problems such as corrosion resistance and location of the diamond. Brazing pastes known in the art fail to address the problem of varying thermal expansion rates in the brazing of diamond to steel.

The brazing of electrical contact material to its supporting structure also presents similar problems with dissimilar thermal expansion rates. Electrical contact material is generally a silver or silver-cadmium oxide alloy, an example of such a material is disclosed in U.S. Patent No. 4,700,475. Another common electrical contact material is tungsten carbide impregnated with silver. The supporting structure for the electrical contact is often made of copper or steel.

It is therefore desirable to provide a brazing paste which will provide a superior quality joint and can compensate for thermal stresses created in the brazing of materials with dissimilar thermal expansion rates, and which may be used in normal commercial brazing operations, such as brazing by torch or induction.

SUMMARY

Accordingly, the brazing paste of the present invention includes a powdered metal brazing alloy, powdered metal spheres made of a material such as stainless steel that will not be drawn into solution by the brazing alloy, an inorganic flux and a binder material to provide a paste-like consistency. A brazing paste with this composition is equally well suited for brazing by directly applied heating techniques such as torch or induction and works especially well when brazing carbide to steel, diamond to steel, or electrical contact materials to steel or copper.

DETAILED DESCRIPTION OF THE INVENTION

While the invention is described in connection with particular embodiments, it will be understood that it is not intended to limit the invention to these embodiments. On the contrary, it is intended to cover all alter-

natives, modifications and equivalents as may be included in the spirit and scope of the invention as defined by the claims.

The brazing paste according to the invention comprises four basic components: a brazing alloy, a powdered metal spacer, an inorganic flux and a binder material to provide a paste-like consistency.

The brazing alloy is a powdered metal alloy, the exact composition can depend on the particular materials being joined. Three compositions of brazing alloy which work particularly well in the brazing of steel and carbide, diamond or electrical contact material are: 45Ag - 15Cu - 16Zn - 24Cd; 50Ag - 15.5Cu - 15.5Zn - 16Cd - 3Ni, and 50Ag - 20Cu - 28Zn - 2Ni. The numbers preceding the element symbols refer to the weight percent of that particular element in the alloy mixture. Brazing alloys based on silver, copper and zinc are generally preferable because of their relatively lower melting points, in the range of 1100 to 1450°F depending on the particular percentages and other alloys included. Some other additional elements which might be included in the alloy are manganese, tin or phosphorous.

The powdered metal spacer is a critical component of the brazing paste because it provides a buffer between the parts being joined which compensates for thermal stresses developed during the brazing process. The powdered metal spacer is formed by known powdered metal technology, i.e., atomizing and screening to select the desired size particles. The particles in the form of spheres should be sized to provide the optimum gap between the parts to be joined. Generally, for the applications discussed this is approximately 0.003 inches. Depending on the particular application the ideal size may vary within a range of about 0.0029-0.005 inches in diameter for spheres. At gaps beyond 0.005 inches joint strength becomes reduced

and gaps below 0.0029 inches are generally not large enough to provide the necessary stress relief. The size of the spheres is to be large enough so that when the materials being brazed together are pressed and held together during the brazing operation, the spheres function to hold the materials spaced from each other and prevent the paste and alloy from being squeezed out.

The powdered metal spacer should be provided in a quantity sufficient to maintain the desired gap in all areas of the joint. A quantity of spacer equal to 3% by weight of all metal components of the paste has been found to give excellent results. The quantity may be varied in the range of 0.5-12% by weight of the metal components of the paste. An excessive quantity of spacer metal will weaken the joint by actually reducing the brazed area, and inadequate amount of spacer may lead to the development of thermal stress and resulting cracks.

The material selected for the spacer should be a ductile metal with a melting point higher than that of the brazing alloys. But it is also necessary that the metal selected be one which will maintain its size during the brazing operation and not be drawn into solution by the brazing alloy at the brazing temperature, even if that temperature is below the actual melting point of the spacer metal. For this reason metals such as nickel or copper are not suitable as spacer metals. Stainless steel, however, provides a good combination of ductility, high melting point and resistance to being drawn into solution. The only additional requirement is that the metal selected as spacer be wettable by the brazing alloy in order to provide maximum joint strength. AISI 316 stainless steel is an example of a spacer metal which exhibits the necessary properties and creates a good joint.

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The flux is an important component of the brazing paste because it permits the paste to be used in torch or induction brazing operations. The flux acts as a cleansing agent to remove oxides which would inhibit the creation of a brazed joint. Suitable fluxes are commercially available which consist of inorganic chemicals such as boric acid, fluorides and borates.

The binder material holds the components together and gives the brazing paste its paste-like consistency, between 250,000 cps and 1,000,000 cps. This consistency allows the brazing paste to be applied by existing automated dispensing equipment. The binder material is made up of a polymer and a solvent such as mineral spirits and water. An emulsifier may be added to the binder material if required for the particular application.

A brazing paste formulated as above has been found to be effective in brazing carbide to steel, diamond to steel, and electrical contact silver and silver-cadmium oxide or tungsten carbide to steel or copper by directly applied heating means such as torch, induction, electrical resistance or laser brazing. These are materials commonly joined in commercial applications, however, the present invention is not limited to joining only these materials. The present invention is generally suitable for brazing together materials having dissimilar thermal expansion rates. Materials having dissimilar thermal expansion rates, as used herein, contemplates materials which traditionally have been or could have been joined by brazing, but the differences in their thermal properties prevented the creation of a successful joint.

The method for creating a brazed joint using the present invention is explained below in terms of carbide and steel alone for reasons of simplicity, but it applies equally to any of the materials disclosed above. The joint

area of both parts must be cleaned to remove oil and dirt, etc., then a small amount of brazing paste is placed on each major surface plane of steel which is to be brazed. The spacer material must be spread evenly in all areas of the joint because it will not flow as does the brazing alloy. The carbide part to be brazed is then pressed firmly into place. Excess brazing paste which is forced from the joint should be removed prior to heating. Next, heat is applied directly to the joint area by torch or induction coil. Heating should be accomplished as quickly as possible, without overheating. By way of example the brazing temperature for the Ag-Cu-Zn-Cd brazing alloy disclosed above is approximately 1145°F. Temperatures should be altered in accordance with the particular brazing alloy used. After the proper heating is complete, the joint should be allowed to cool in still air.

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WHAT IS CLAIMED IS:

1. A brazing paste for joining materials having dissimilar thermal expansion rates, comprising:
 - 5 (a) a powdered metal brazing alloy;
 - (b) ductile powdered metal spheres comprising 0.5-12% by weight of the metal components of the paste, the powdered metal spheres being a material which will not be brought into solution by the brazing alloy at the brazing
10 temperature;
 - (c) an inorganic flux material; and
 - (d) a binder material.
2. The brazing paste as in claim 1, wherein:
 - 15 (a) the powdered metal brazing alloy is a mixture which includes silver and copper; and
 - (b) the powdered metal spheres are stainless steel, and have a diameter between about .0029-.005 inches.
3. The brazing paste as in claim 2, wherein:
 - 20 (a) the stainless steel spheres have a diameter of approximately .003 inches and make up about 3% by weight of the metal components of the paste.
4. A method of brazing together carbide and
25 steel, which includes the step of placing between the carbide and steel a brazing paste, comprising:
 - (a) a powdered metal brazing alloy;
 - (b) a plurality of ductile powdered metal
30 spheres made of a material which will not be brought into solution by the brazing alloy at the brazing temperature, the spheres having a diameter in the range of approximately .0029-.005 inches and comprising 1-12% by weight of the metal components of the paste;
 - 35 (c) an inorganic flux material; and

(d) a binder material.

5. The method as in claim 4, further comprising the step of:

5 (a) heating the paste by torch to form a brazed joint.

6. The method as in claim 4, further comprising the step of:

10 (a) heating the paste by induction coil to form a brazed joint.

7. A method of brazing together diamond and steel, which includes the step of placing between the
15 diamond and steel a brazing paste, comprising:

(a) a powdered metal brazing alloy;
(b) a plurality of ductile powdered metal
spheres made of a material which will not be brought into
solution by the brazing alloy at the brazing temperature,
20 the spheres having a diameter in the range of approximately
.0029-.005 and comprising 1-12% by weight of the metal
components of the paste;

(c) an inorganic flux material; and

(d) a binder material.

25 8. The method as in claim 7, further comprising the step of:

(a) heating the paste by torch to form a brazed joint.

30 9. The method as in claim 7, further comprising the step of:

(a) heating the paste by induction coil to form a brazed joint.

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10. A method of brazing together electrical contact material and a metal selected from a group consisting of steel and copper which includes the step of placing between the electrical contact material and the metal a
5 brazing paste, comprising:

- (a) a powdered metal brazing alloy;
- (b) a plurality of ductile powdered metal spheres made of a material which will not be brought into solution by the brazing alloy at the brazing temperature,
10 the spheres having a diameter in the range of approximately .0029-.005 inches and comprising 1-12% by weight of the metal components of the paste;
- (c) an inorganic flux material; and
- (d) a binder material.

15 11. The method as in claim 10, further comprising the step of:

- (a) heating the paste by torch to form a brazed joint.

20 12. The method as in claim 10, further comprising the step of:

- (a) heating the paste by induction coil to form a brazed joint.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04721

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC <div style="display: flex; justify-content: space-around; margin-top: 5px;"> INT. C1(4) B23K 35/28 </div>																													
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 5px;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <th style="width: 20%;">Classification System</th> <th>Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">U.S.</td> <td>228/248, 122, 123, 180.2, 189, 263.12 148/ 23, 24</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	228/248, 122, 123, 180.2, 189, 263.12 148/ 23, 24																							
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%;">Category [*]</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">X Y</td> <td>DE, A, 27 35 638 (FUSION INC) 15 FEBRUARY 1979, See English abstract.</td> <td style="text-align: center; vertical-align: top;">1-3 4-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,431,465 (MIZUHARA ET AL) 14 FEBRUARY 1984, See entire specification.</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,900,153 (BEERWERTH ET AL) 19 AUGUST 1975, See entire specification.</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,731,130 (O'LEARY) 15 MARCH 1988, See column 2.</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,740,252 (HASEGAWA ET AL) 26 APRIL 1988, See Table 1.</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>METALS HANDBOOK NINTH EDITION, Vol. 6, pp. 950-975, Copyright 1983.</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 3,856,480 (JOHNSON ET AL) 24 DECEMBER 1974</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4,650,107 (KESER) 17 MARCH 1987</td> <td></td> </tr> </table> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div> </div>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X Y	DE, A, 27 35 638 (FUSION INC) 15 FEBRUARY 1979, See English abstract.	1-3 4-12	Y	US, A, 4,431,465 (MIZUHARA ET AL) 14 FEBRUARY 1984, See entire specification.	1-12	Y	US, A, 3,900,153 (BEERWERTH ET AL) 19 AUGUST 1975, See entire specification.	1-12	Y	US, A, 4,731,130 (O'LEARY) 15 MARCH 1988, See column 2.	1-12	Y	US, A, 4,740,252 (HASEGAWA ET AL) 26 APRIL 1988, See Table 1.	1-12	Y	METALS HANDBOOK NINTH EDITION, Vol. 6, pp. 950-975, Copyright 1983.	1-12	A	US, A, 3,856,480 (JOHNSON ET AL) 24 DECEMBER 1974		A	US, A, 4,650,107 (KESER) 17 MARCH 1987	
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IV. CERTIFICATION <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> Date of the Actual Completion of the International Search 04 DECEMBER 1989 </td> <td style="width: 50%; vertical-align: top;"> Date of Mailing of this International Search Report <div style="font-size: 1.5em; font-weight: bold;">19 JAN 1990</div> </td> </tr> <tr> <td style="vertical-align: top;"> International Searching Authority ISA/US </td> <td style="vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> SAMUEL M. HEINRICH </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 04 DECEMBER 1989	Date of Mailing of this International Search Report <div style="font-size: 1.5em; font-weight: bold;">19 JAN 1990</div>	International Searching Authority ISA/US	Signature of Authorized Officer <div style="text-align: center;"> SAMUEL M. HEINRICH </div>																							
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,319,707 (KNEYMEYER) 16 MARCH 1982
A	US, A, 4,560,853 (ZIEGEL) 24 DECEMBER 1985
A	US, A, 4,769,525 (LEATHAM) 06 SEPTEMBER 1988
A	JP, A, 55-54262 (HITACHI SEISAKUSHO K.K.) 21 APRIL 1980

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.